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Interner Bericht

Calculation of Chemical Equilibrium Compositions

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This worksheet will be published in a collection of application on worksheets for the next Maple release.

Calculation of Chemical Equilibrium Compositions

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The catalytic reaction between steam and hydrocarbon into mixtures of hydrogen, carbon monoxide, carbon dioxide and methane forms the basic feedstock (synthesis gas) to produce ammonia, methanol and other chemicals. For reactor design and to find the most economic reaction conditions it is necessary to study theoretically the reaction behaviour with respect to the operating parameters. In the present thermodynamic study we examine the temperature dependence of chemical compositions at equilibrium. We consider the following simple system of steam reforming reactions:

1. The methane-steam equality

CH4 + H2O <-> CO + 3H2

2. The water-gas shift

CO + H2O <-> CO2 + H2

To set up a practical computation model we formulate the equilibrium condition for each separate reaction in terms of the reaction extents xi[1] and xi[2]. If ne[j] is the number of moles of chemical species B[j] (j=1..5) present at equilibrium and n[j] is the initial number of moles of that species, then

```
> ne[j] = n[j]+Sum(alpha[j,i]*xi[i], i=1..2);
```

$$ne_{[j]} = n_{[j]} + \left(\sum_{i=1}^{2} \alpha_{[j,i]} \xi_{[i]} \right)$$

holds, where alpha[i,j] are the stoichiometric coefficients of species B[j] in each of the equations (i) [O&W, 80]. The matrix of stoichiometric coefficients for these molecular mass balance equations is given by

```
> with(linalg):
  alpha := matrix ([[-1, 0], [-1, -1], [1, -1], [3, 1], [0, 1]]);
```
Warning: new definition for norm
Warning: new definition for trace

$$\alpha := \begin{bmatrix} -1 & 0 \\ -1 & -1 \\ 1 & -1 \\ 3 & 1 \\ 0 & 1 \end{bmatrix}$$

A feed mixture of n[1] moles of methane with n[2] moles of steam results in the following composition of the participating components at equilibrium:

```
> xi := vector(2): print(xi);
  n  := vector(5): for k from 3 to 5 do n[k]:=0 od: print(n);
  ne := add(n, multiply (alpha, xi));
```

$$\left[\xi_{[1]} \; \xi_{[2]}\right]$$

$$\left[n_{[1]} \; n_{[2]} \; 0 \; 0 \; 0\right]$$

$$ne := \left[n_{[1]} - \xi_{[1]} \; n_{[2]} - \xi_{[1]} - \xi_{[2]} \; \xi_{[1]} - \xi_{[2]} \; 3\,\xi_{[1]} + \xi_{[2]} \; \xi_{[2]}\right]$$

The equilibrium constants of the reactions in terms of the partial pressures

```
> p := vector([P[CH4], P[H2O], P[CO], P[H2], P[CO2]]);
```

$$p := \left[P_{[CH4]} \; P_{[H2O]} \; P_{[CO]} \; P_{[H2]} \; P_{[CO2]}\right]$$

are calculated by

```
> for i from 1 to 2 do
      eqn[i] := K[i] = Product(p[j]^alpha[j,i], j=1..5);
      print(");
      print(value("));
  od:
```

$$K_{[1]} = \prod_{j=1}^{5} p_{[j]}^{\alpha_{[j,1]}}$$

$$K_{[1]} = \frac{P_{[CO]} P_{[H2]}^{3}}{P_{[CH4]} P_{[H2O]}}$$

$$K_{[2]} = \prod_{j=1}^{5} p_{[j]}^{\alpha_{[j,2]}}$$

$$K_{[2]} = \frac{P_{[H2]} P_{[CO2]}}{P_{[H2O]} P_{[CO]}}$$

Now, if we insert the relation p[j] = x[j]*P, where p[j] denotes the partial pressure, P the total pressure and x[j] the mole fraction of chemical component B[j], then we obtain

```
> for j from 1 to 5 do
      p[j] := x[j] * P
  od:
  j:='j':
  for i from 1 to 2 do
      print(value(eqn[i]));
  od:
```

$$K_{[1]} = \frac{P^2 x_{[3]} x_{[4]}^{\,3}}{x_{[1]} x_{[2]}}$$

$$K_{[2]} = \frac{x_{[4]} x_{[5]}}{x_{[2]} x_{[3]}}$$

The individual mole fractions x[j] are calculated by dividing ne[j] by the total number of moles. Thus, the sum over the component index should yield unity.

```
> nsum := sum(ne[j], j=1..5);
  x    := map (y -> y/nsum, ne);
  Sum(x[j], j=1..5) = simplify(sum(x[j], j=1..5));
```

$$nsum := n_{[1]} + 2\,\xi_{[1]} + n_{[2]}$$

$$x := \left[\frac{n_{[1]} - \xi_{[1]}}{\%1} \quad \frac{n_{[2]} - \xi_{[1]} - \xi_{[2]}}{\%1} \quad \frac{\xi_{[1]} - \xi_{[2]}}{\%1} \quad \frac{3\,\xi_{[1]} + \xi_{[2]}}{\%1} \quad \frac{\xi_{[2]}}{\%1} \right]$$

$$\%1 := n_{[1]} + 2\,\xi_{[1]} + n_{[2]}$$

$$\sum_{j=1}^{5} x_{[j]} = 1$$

The equilibrium mixture defined by xi[1] and xi[2] must simultaneously satisfy the equilibrium condition for each reaction, i.e. we have to solve the following equations for the reaction extents simultaneously:

```
> for i from 1 to 2 do
      f[i] := ln(value(rhs(eqn[i]))) - ln(lhs(eqn[i]))=0;
      print(");
  od:
```

$$\ln\left(\frac{P^2\left(\xi_{[1]}-\xi_{[2]}\right)\left(3\,\xi_{[1]}+\xi_{[2]}\right)^3}{\left(n_{[1]}-\xi_{[1]}\right)\left(n_{[1]}+2\,\xi_{[1]}+n_{[2]}\right)^2\left(n_{[2]}-\xi_{[1]}-\xi_{[2]}\right)}\right)-\ln\left(K_{[1]}\right)=0$$

$$\ln\left(\frac{\left(3\,\xi_{[1]}+\xi_{[2]}\right)\xi_{[2]}}{\left(n_{[2]}-\xi_{[1]}-\xi_{[2]}\right)\left(\xi_{[1]}-\xi_{[2]}\right)}\right)-\ln\left(K_{[2]}\right)=0$$

Before solving this system of nonlinear equations we determine the temperature dependence of the constants K[1] and K[2]. To obtain an expression for the reaction enthalpy we apply Kirchhoff's law with a polynomial ansatz for the description of the molar heat capacity. We have

```
> diff(H[P](T), T) = sum(A[j]*(s*T)^j, j=0..6);
  expand(dsolve(", H[P](T)));
  assign(");
```

$$\frac{\partial}{\partial T}H_{[P]}(T)=A_{[0]}+A_{[1]}\,s\,T+A_{[2]}\,s^2\,T^2+A_{[3]}\,s^3\,T^3+A_{[4]}\,s^4\,T^4+A_{[5]}\,s^5\,T^5+A_{[6]}\,s^6\,T^6$$

$$H_{[P]}(T)=A_{[0]}\,T+\frac{1}{2}A_{[1]}\,s\,T^2+\frac{1}{3}A_{[2]}\,s^2\,T^3+\frac{1}{4}A_{[3]}\,s^3\,T^4+\frac{1}{5}A_{[4]}\,s^4\,T^5+\frac{1}{6}A_{[5]}\,s^5\,T^6+\frac{1}{7}A_{[6]}\,s^6\,T^7+\_C1$$

Here, s (=10^(-3)) denotes a scaling factor of the temperature T as used in thermochemical tables. Inserting the expression for H[P](T) into the equation of van't Hoff and then integrating yields

```
> diff(lnK[P](T),T)='H[P](T)'/(R*T^2);
  expand(dsolve(", lnK[P](T)));
  assign(");
```

$$\frac{\partial}{\partial T}lnK_{[P]}(T)=\frac{H_{[P]}(T)}{R\,T^2}$$

$$lnK_{[P]}(T)=\frac{1}{42}\frac{A_{[6]}\,s^6\,T^6}{R}+\frac{1}{30}\frac{A_{[5]}\,s^5\,T^5}{R}+\frac{1}{20}\frac{A_{[4]}\,s^4\,T^4}{R}+\frac{1}{12}\frac{A_{[3]}\,s^3\,T^3}{R}+\frac{1}{6}\frac{A_{[2]}\,s^2\,T^2}{R}+\frac{1}{2}\frac{A_{[1]}\,s\,T}{R}+\frac{A_{[0]}\ln(T)}{R}-\frac{\_C1}{R\,T}+\_C2$$

The coefficients A[j] are determined by the corresponding coefficients of the pure substances in each reaction [Pro, 69].

```
> U0:=matrix([[a0[CH4], a0[H2O], a0[CO], a0[H2], a0[CO2]],
              [a1[CH4], a1[H2O], a1[CO], a1[H2], a1[CO2]],
              [a2[CH4], a2[H2O], a2[CO], a2[H2], a2[CO2]],
              [a3[CH4], a3[H2O], a3[CO], a3[H2], a3[CO2]],
              [a4[CH4], a4[H2O], a4[CO], a4[H2], a4[CO2]],
              [a5[CH4], a5[H2O], a5[CO], a5[H2], a5[CO2]],
              [a6[CH4], a6[H2O], a6[CO], a6[H2], a6[CO2]]]);
```

$$U0 := \begin{bmatrix} a0_{[CH4]} & a0_{[H2O]} & a0_{[CO]} & a0_{[H2]} & a0_{[CO2]} \\ a1_{[CH4]} & a1_{[H2O]} & a1_{[CO]} & a1_{[H2]} & a1_{[CO2]} \\ a2_{[CH4]} & a2_{[H2O]} & a2_{[CO]} & a2_{[H2]} & a2_{[CO2]} \\ a3_{[CH4]} & a3_{[H2O]} & a3_{[CO]} & a3_{[H2]} & a3_{[CO2]} \\ a4_{[CH4]} & a4_{[H2O]} & a4_{[CO]} & a4_{[H2]} & a4_{[CO2]} \\ a5_{[CH4]} & a5_{[H2O]} & a5_{[CO]} & a5_{[H2]} & a5_{[CO2]} \\ a6_{[CH4]} & a6_{[H2O]} & a6_{[CO]} & a6_{[H2]} & a6_{[CO2]} \end{bmatrix}$$

```
> U:=subs(a0[CH4]=7.918404, a0[H2O]=7.988860,   a0[CO]=7.812249,
          a0[H2]=6.183042, a0[CO2]=4.324933,
          a1[CH4]=-11.41722, a1[H2O]=-1.506271, a1[CO]=-6.668293,
          a1[H2]=4.710657, a1[CO2]=20.80895,
          a2[CH4]=63.73457, a2[H2O]=6.661376, a2[CO]=17.28296,
          a2[H2]=-10.92135, a2[CO2]=-22.94590,
          a3[CH4]=-75.25691, a3[H2O]=-4.655970, a3[CO]=-17.28709,
          a3[H2]=12.54086, a3[CO2]=16.84483,
          a4[CH4]=43.29269, a4[H2O]=1.696464, a4[CO]=8.860125,
          a4[H2]=-7.016263, a4[CO2]=-7.935665,
          a5[CH4]=-12.56732, a5[H2O]=-0.3706212, a5[CO]=-2.314819,
          a5[H2]=1.923395, a5[CO2]=2.121672,
          a6[CH4]=1.469695, a6[H2O]=0.03992444, a6[CO]=0.2447785,
          a6[H2]=-0.2084091, a6[CO2]=-0.2408713, eval(U0));
```

$$U := \begin{bmatrix} 7.918404 & 7.988860 & 7.812249 & 6.183042 & 4.324933 \\ -11.41722 & -1.506271 & -6.668293 & 4.710657 & 20.80895 \\ 63.73457 & 6.661376 & 17.28296 & -10.92135 & -22.94590 \\ -75.25691 & -4.655970 & -17.28709 & 12.54086 & 16.84483 \\ 43.29269 & 1.696464 & 8.860125 & -7.016263 & -7.935665 \\ -12.56732 & -.3706212 & -2.314819 & 1.923395 & 2.121672 \\ 1.469695 & .03992444 & .2447785 & -.2084091 & -.2408713 \end{bmatrix}$$

```
> V:=multiply(U,alpha);
```

$$V := \begin{bmatrix} 10.454111 & -5.293134 \\ 20.387169 & 33.694171 \\ -85.877036 & -57.811586 \\ 100.248370 & 51.328750 \\ -57.177818 & -25.508517 \\ 16.3933072 & 6.7305072 \\ -1.89006824 & -.73398334 \end{bmatrix}$$

The integration constants _C1 and _C2 can be calculated by using special values for K[1] and K[2] at the temperature T=298.15 Kelvin [Bar, 93]. Inserting the value for the gas constant R and taking into account the conversion factor F between the unit cal (used in Prothero's termochemical table [Pro, 69]) and the SI unit Joule we eventually arrive at:

```
> R:=8.314: H[1]:=206185: H[2]:=-41165: lnK[1]:=-57.3621:
  lnK[2]:=11.546: s:=10^(-3): F:=4.1868:


> for i from 1 to 2 do
      for k from 0 to 6 do
          A[k]:=F*V[k+1, i]
      od;
      solve({H[i]=subs(T=298.15, H[P](T))},_C1);
      print(op("));assign(");
      solve({lnK[i]=subs(T=298.15,lnK[P](T))},_C2);
      print(op("));assign(");
      ln(K[i])=eval(lnK[P](T));
      print(");assign(");
      _C1:='_C1':_C2:='_C2':
  od:
```

$$\_C1 = 191793.6485$$

$$\_C2 = -10.97479514$$

$$\ln\left(K_{[1]}\right) = -.2266211241\ 10^{-19}\ T^6 + .2751804129\ 10^{-15}\ T^5 - .1439692618\ 10^{-11}\ T^4 + .4206958900\ 10^{-8}\ T^3 - .7207721401\ 10^{-5}\ T^2 + .005133329275\ T + 5.264526333 \ln(T) - 23068.75734 \frac{1}{T} - 10.97479514$$

$$\_C1 = -39066.81111$$

$$\_C2 = 8.82248534$$

$$\ln\left(K_{[2]}\right) = -.8800535667\ 10^{-20}\ T^6 + .1129792621\ 10^{-15}\ T^5 - .6422844540\ 10^{-12}\ T^4 + .2154029453\ 10^{-8}\ T^3 - .4852167998\ 10^{-5}\ T^2 + .008483928020\ T - 2.665539263 \ln(T) + 4698.918825 \frac{1}{T} + 8.82248534$$

Thus, the complete expressions for the reactions extents xi[1] and xi[2] are given by

```
> f1:=lhs(f[1]); f2:=lhs(f[2]);
```

$$f1 := \ln\left(\frac{P^2 \left(\xi_{[1]} - \xi_{[2]}\right)\left(3\,\xi_{[1]} + \xi_{[2]}\right)^3}{\left(n_{[1]} - \xi_{[1]}\right)\left(n_{[1]} + 2\,\xi_{[1]} + n_{[2]}\right)^2 \left(n_{[2]} - \xi_{[1]} - \xi_{[2]}\right)}\right) + .2266211241\ 10^{-19}\ T^6 - .2751804129\ 10^{-15}\ T^5 + .1439692618\ 10^{-11}\ T^4 - .4206958900\ 10^{-8}\ T^3 + .7207721401\ 10^{-5}\ T^2 - .005133329275\ T - 5.264526333 \ln(T) + 23068.75734 \frac{1}{T} + 10.97479514$$

$$f2 := \ln\left(\frac{\left(3\,\xi_{[1]} + \xi_{[2]}\right)\xi_{[2]}}{\left(n_{[2]} - \xi_{[1]} - \xi_{[2]}\right)\left(\xi_{[1]} - \xi_{[2]}\right)}\right) + .8800535667\ 10^{-20}\ T^6 - .1129792621\ 10^{-15}\ T^5 + .6422844540\ 10^{-12}\ T^4 - .2154029453\ 10^{-8}\ T^3 + .4852167998\ 10^{-5}\ T^2 - .008483928020\ T + 2.665539263 \ln(T) - 4698.918825 \frac{1}{T} - 8.82248534$$

Next, we assume P=5 bar and a steam to carbon atom ratio H2O : C = 2:1, i.e.

```
> P:=5; n[1]:=1; n[2]:=2;
```

$$P := 5$$

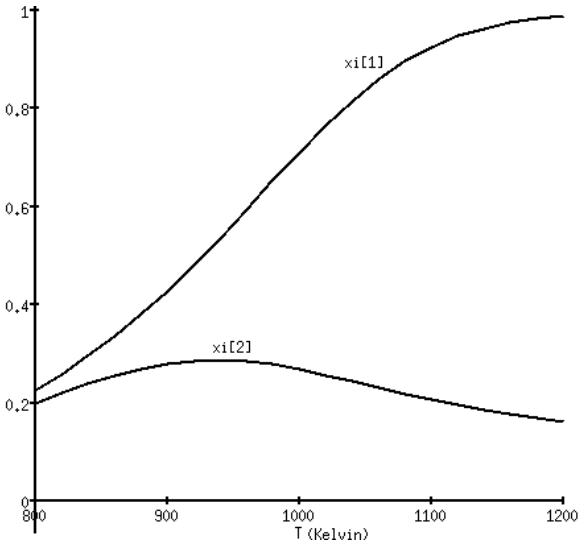
$$n_{[1]} := 1$$

$$n_{[2]} := 2$$

Now, solving the nonlinear equations for xi[1] and xi[2] at different values of T (800..1200 Kelvin) results in the following temperature dependence of the reaction extents and of the various mole fractions for steam, hydrogen, carbon monoxide, carbon dioxide, and methane.

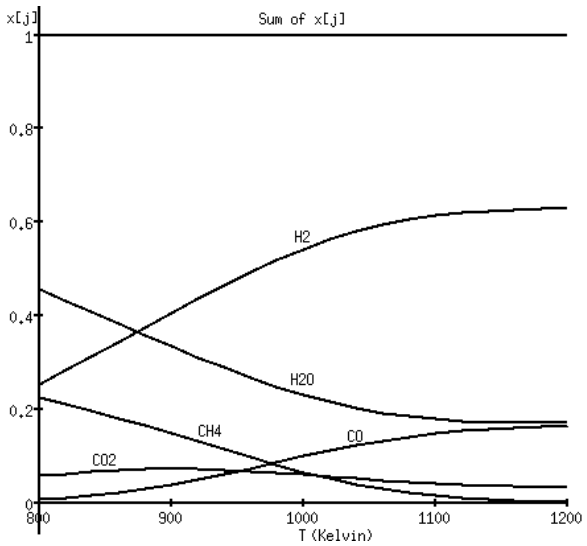
```
> for k from 1 to 2 do l1[k]:=NULL od:
  for k from 1 to 5 do l2[k]:=NULL od:
```

```
> for j from 0 to 20 do
      T := 800 + j*20:
      fsolve({f1, f2}, {xi[1], xi[2]}, {xi[1]=0.2..1,
              xi[2]=0.12..0.3});
      assign(");
      xiT:=map(eval, xi);
      for k from 1 to 2 do
          l1[k] := l1[k], [T, xiT[k]];
      od;
      xT:=map(eval, x);
      for k from 1 to 5 do
          l2[k] := l2[k], [T, xT[k]];
      od;
      xi[1]:='xi[1]'; xi[2]:='xi[2]';
  od:

> with(plots): T:='T':

> pl1:=plot({seq([l1[k]], k=1..2)}, T=800..1200):

> t1[1]:=textplot([1050, 0.88, 'xi[1]'], align=ABOVE):
  t1[2]:=textplot([950, 0.3, 'xi[2]'], align=ABOVE):
  t1[3]:=textplot([1030, -0.045, '(Kelvin)'], align=BELOW):

> display({pl1, seq(t1[i], i=1..3)});
```




```
> pl2:=plot({seq([l2[k]], k=1..5), 1}, T=800..1200):

> t2[1]:=textplot([930, 0.14, 'CH4'], align=ABOVE):
  t2[2]:=textplot([1000, 0.25, 'H2O'], align=ABOVE):
  t2[3]:=textplot([1040, 0.13, 'CO'], align=ABOVE):
  t2[4]:=textplot([1000, 0.555, 'H2'], align=ABOVE):
  t2[5]:=textplot([850, 0.08, 'CO2'], align=ABOVE):
  t2[6]:=textplot([1000, 1.02, 'Sum of x[j]'], align=ABOVE):
  t2[7]:=textplot([800, 1.04, 'x[j]'], align=LEFT):
  t2[8]:=textplot([1030, -0.045, '(Kelvin)'], align=BELOW):
```

```
> display({pl2, seq(t2[i], i=1..8)});
```



References

[O&W, 80] A. Ovenston and J.R. Walls, Chem. Engineering Sci. 35, 627-633, (1980).

[Pro, 69] A. Prothero, Comb. Flame. 13, 399-408, (1969).

[Bar, 93] I. Barin ‘‘Thermochemical Data of Pure Substances’’, VCH Verlagsgesellschaft, Weinheim (1993).